NASA
CR189214

AVSCOM
Technical Report 92-C-032

WEAR REDUCTION IN CERAMIC BEARINGS BY SURFACE GENERATED PYROLYTIC CARBON CONTINUOUSLY REPLENISHED BY ETHYLENE GAS

Dr. J. L. Lauer — Rensselaer Polytechnic Institute
L. C. Davis — Allison Gas Turbine Div. GM

December 13, 1993

Prepared for the
Lewis Research Center
Under Contract NAS3-25950 Task 3

Ref. EDR 16732

ERRATA
for NASA CR-189214

Wear Reduction in Ceramic Bearings by
Surface Generated Pyrolytic Carbon
Continuously Replenished by Ethylene Gas

by

Dr. J. L. Lauer
L. C. Davis

The last sentence at the bottom of page 15, and the first sentence at the top of page 16 should read as follows:

The two principal Raman bands of carbon have been called D (the low frequency band at about 1360 cm^{-1}, D for diamond or disorder), and G (the high frequency band at about 1600 cm^{-1}, G for graphite). A strong D band compared to the G band has been considered evidence of small graphite-like crystallites.

TABLE OF CONTENTS

SYNOPSIS

Sliding tests with a pin-on-disc tribometer and both sliding and rolling tests with a modified four-ball tester at bulk temperatures of about 500°C and contact pressures of about 2.2 GPa have demonstrated up to 80% reductions of friction and wear with silicon nitride surfaces when a stream of ethylene is directed into the conjunction region. The effects are even more pronounced when the ethylene is prenucleated by a flow over a coil of nichrome wire electrically heated to about 800°C and located about 30 cm upstream of the exit nozzle. Steel and Ni-plated steel are lubricated by this method even more efficiently at lower temperatures. The underlying mechanism is probably analogous to that of hydrocarbon pyrolysis by flash photolysis, which was studied by Porter in the 1950's, with the rapid heating to the "flash temperatures" and subsequent cooling occurring naturally in friction contacts. The observation that pyrolysis of hydrocarbons to solid carbon occurs in two stages, nucleation and particle growth, has allowed their physical separation, with nucleation taking place in the ethylene stream and particle growth in the frictional contact some distance away.

To get these results it was necessary to modify our pin-on-disc tester to accommodate the high pressures and temperatures and rebuild the four-ball tester kindly donated to us by Allison. The four-ball tester required instrumentation to measure friction as a function of torque, and a means to switch from sliding to rolling friction. It was also furnished with a test chamber containing three flats instead of the three lower balls, a replacement necessitated by the high cost of ceramic parts (flats can be repolished and reused, but balls can be used only once). However, the flats can be used only in sliding experiments. Both testers were provided with appropriate heaters and safe means for the introduction of the potentially dangerous ethylene gas.

All the tests proposed have been completed; lubrication of hot ceramic surfaces in both sliding and rolling has been demonstrated at high contact pressures, and significant progress toward a prototype lubrication system has been made during this project.

INTRODUCTION

Gas turbine engines require high quality rolling element bearings to run at high speeds, loads, and temperatures. Integrated high performance turbine engine technology (IHPTET) engines will require bearing operation at 1200°F - 1500°F. Allison requires this capability for their advanced turbine engine gas generator (ATEGG), ETEC and future joint technology demonstrator engine (JTDE) programs. For high efficiency these bearing should also be light. Ceramic bearings would be ideally suited for this application were it not for their predisposition to fatigue, fracture, and other modes of failure and their high friction and wear rates. Lubricants can help minimize these difficulties.

At temperatures about 400°C, (750°F) lubrication by liquids, which can be replenished by conventional means, is probably impossible. Solid lubricants however, will need unusual methods of replenishment. Methods suggested include the following:

- stick or powder feed
- gaseous or liquid suspension feed
- incorporation in pockets or retainers
- gaseous materials or suspensions in gases adsorbed by or reacting with the solid surfaces (Klaus)
- gases reacting at the surfaces (RPI)

Gases have an obvious advantage in ease of replenishment with regard to transport, injection, transfer, build-up and scavenge.

Research at Rensselaer Polytechnic Institute (RPI) over the past several years has established that it is possible to lubricate, catalytically or tribochemically, active bearing surfaces at 350°C - 650°C by continuous generation of a carbonaceous solid directly on the surfaces from a carbon-containing thermally stable gas such as ethylene. Both friction and wear have been reduced drastically from the unlubricated values in a pin-on-disc tribometer.

The purpose of this joint program of RPI with Allison Gas Turbine, was to apply this concept to gas turbine bearings under realistic engine conditions. Four-ball tests were to be conducted on silicon nitride bearings with and without nickel or palladium catalytic coatings. Detailed analytical procedures by the latest appropriate methods were to make it possible to obtain accelerated data for the design of the best materials and configuration. Atmospheres, temperatures, speed and loads were to be varied.

The objective of this research project was to demonstrate the applicability of our concept of high temperature lubrication by carbon formed at the tribo-surfaces from a continuous feed of a carbonaceous gas. Our earlier work (1) had shown that very significant reductions of friction and some reductions of wear were possible by this method, both with metallic and with ceramic (sialon and sapphire) pin-on-disc contacts at temperatures between 350° and 650°C, but only in the low contact pressure range of about 200 MPa. Therefore, the program of research described here focused on the more realistic contact pressures of 2.2 to 2.5 GPa, on silicon nitride surfaces and on wear as well as on friction measurements, but primarily on wear. For this purpose our pin-on-disc tester had to be modified and a four-ball wear tester kindly donated to us by Allison Gas Turbine Division of General Motors Corporation had to be rebuilt to bring it into the required temperature range, to allow both rolling and sliding friction and wear measurements and to enable the introduction of ethylene as a representative carbonaceous gas into the test section. Since ethylene and most other carbonaceous (organic) gases are highly flammable when exposed to air or oxygen in the required temperature region, safety concerns had to be of foremost importance. Fortunately no safety problems were encountered but our progress was certainly slowed on that account.

BACKGROUND

Initial experiments with the pin-on-disc tester modified for higher contact pressures by the substitution of small diameter silicon nitride balls (generally 3 mm diameter) for the sapphire pins and the substitution of silicon nitride discs for the sialon discs were only marginally successful. Clearly, more lubricant was needed at the higher than at the lower pressures. But when more ethylene gas, our primary source of lubricant, was introduced into the contact region, the quartz halogen lamp used as a heat source would become coated with carbon and fail rapidly. Therefore another method of heating the test section became necessary and an enclosure containing coiled electric resistance wires provided the answer. Friction and wear reduction were achieved with ethylene, but generally not as dramatically as at low pressures except for nickel-plated steel surfaces used in control experiments.

For these reasons our basic concept had to be re-examined. Steel and especially nickel-coated steel could be readily lubricated by carbon from ethylene presumably because of the well-known *catalytic* activity of these surfaces, but silicon nitride surfaces were not lubricated very well at the high contact pressures. Increased ethylene flow did not help and could even be harmful, presumably because it cooled the contacting surfaces.

Carbon can be formed on *non-catalytic* tribo-surfaces because of the temperature pulse, i.e. rapid heating and cooling of the ethylene gas in the contact. This phenomenon has been known for some time. Thus carbon is formed when a hydrocarbon gas containing a small concentration of a light-absorbing nitro-compound is exposed to a flash of light: the temperature of the gas is raised and lowered rapidly. The same result occurs behind shock waves in hydrocarbon gases. "Flash" temperatures must be at least 1000°K and pulse durations less than a second for carbon particles to form. At lower temperatures

and with longer durations polymers will form. According to Porter and Norrish, who discovered these
phenomena [2] (flash photolysis) in the 1950's, the process occurs in the gas phase and is homogeneous, i.e. independent of the nature of the surfaces. However, our previous work [1] and that of others [3] did show surface effects. Flash temperatures of 1000°K and above are not unreasonable for ceramic contacts.

There is another facet to our carbon generation, which was derived from Tesner's extensive research on pyrolytic carbon [4] from gaseous streams: the two-step formation of carbon particles. First carbon is nucleated and then the nuclei are growing and the rates of nucleation and growth are different. The nature of the nuclei is still unknown, but there are a number of hypotheses (C_2, CH+, C_2H_2 in the gas phase and/or a particular carbon deposited on the tribosurfaces). Both stages depend on temperature and on thermal gradient and probably on both. However, the nucleation stage is more likely to be influenced by surface catalysis.

This background provided us with the idea, which was essential to our most recent progress, viz. instead of carrying out both stages in the tribocontact to accomplish most of the nucleation on a heated catalytic surface and the particle growth in the tribo-contact, which would not have to be catalytic, ethylene or other carbonaceous gas flowing over a hot wire surface would provide nucleation and friction in the tribo-contact would provide the required thermal flash of the already nucleated gas.

Neither Porter and Norrish nor Tesner thought of carbon formation in tribocontacts and neither anticipated lubricating properties of the pyrolytic or catalytic carbons formed in their experiments. But the adaptation of their findings to our needs provided us with the breakthrough necessary for progress on the

research described here. Friction and, even more so, wear could be drastically reduced by nucleation of the carbonaceous gas stream at a heated surface upstream of the tribocontact and the subsequent growth of the carbon particles on the surfaces of the tribocontacts. The size and nature of these particles could be estimated by Raman spectroscopy [5].

The following sections contain descriptions of the experimental apparatus and procedures, test results and discussions. The final section contains recommendations on further research needed to bring the concept from the pin-on-disc and four-ball test stages to practical field use.

APPARATUS

Pin-on-disc

Fig. 1 shows our high-temperature pin-on-disc tester for high contact pressures. Ethylene gas is injected into the contact region contained in the inner chamber, which is the test section. The outer chamber provides a safety blanket; it is flushed with argon or other inert gas and it has an unattached cover free to rise in case of an explosion (Ethylene can form explosive mixtures with air or oxygen. However, by diluting it with argon in the inner chamber and replacing the residual air with argon prior to heating the contact region, even mild explosions have been totally avoided). The test section is heated by the coiled resistance heaters shown in Fig. 1. The load and contact pressure of the pin-on-disc tester are controlled by a movable weight on the straining arm. The disc temperature is measured by a sliding thermocouple which was calibrated by a series of paints of known melting points, which were applied to the discs. Originally sapphire pins were used on sialon plates. To increase the contact pressures and use more realistic materials for high-temperature bearing

applications the pins were replaced by a steel holder into which small ceramic balls (silicon nitride balls of 1/8 or 1/16 inch diameter) could be inserted and the plates became 1-inch diameter silicon nitride discs. The initial roughness of these contacts was about 25 μm RMS. Steel and nickel-plated steel (52100 stainless) were used in some experiments for comparison with the ceramics.

While friction is recorded continuously, wear measurements are made only at the end of the experiment when the flattened areas under the pin or ball are measured under the microscope. The carbon clinging to them is wiped off first.

In all cases "lubricated" friction and wear were compared with "unlubricated" friction and wear. Lubricated means lubricated by the pyrolytic carbon deposited on the wear surfaces as a result of ethylene injection.

Typical rotational disc speeds were 69, 128, 178 RPM corresponding to linear speeds of 10,20 and 30 cm/sec. Ethylene (or other carbonaceous gas) flow rates were 0.3, 3.5 and 7 liter/min, contact pressures were between 1.5 and 6.8 GPa, but mostly 2.2 GPa, and the friction couples were silicon nitride against silicon nitride unless otherwise noted.

Four Ball Wear Tester

A standard ASTM Four-Ball Wear Tester (ASTM D2266-67) donated to us by Allison Gas Turbine Division was extensively modified for this work (Fig. 2). It was instrumented to provide automatic friction readouts. The four-ball section was surrounded by a heating mantle containing several cartridge heaters and gas inlet nozzles for ethylene and argon were inserted. A retaining ring was provided to hold the lower three balls stationary for sliding measurements. For rolling friction measurements the retaining ring was removed. The original air piston pressuring method remained but all controls and readouts were moved some

distance away for safety. For safety, automatic shut-off valves were installed as well.

A major modification involved the optional replacement of the lower balls in the test section by plates at appropriate positions and angles. The primary motivation for this change was cost; ceramic balls (1/2 inch diameter) are very expensive and difficult, if not impossible, to repolish after use. Small plates (1/4 inch diameter) are much more reasonable. This modification is basically similar to that of the tester developed by Klaus, Duda and Wu [6].

Heating of the test section required a major effort. We determined early in the project that heating of the entire central part of the unit would require massive power and even then would be impractical because of long heating and cooling times. We therefore concentrated on heating the test section only to a quasi-equilibrium state, i.e. to a temperature that could be maintained long enough for an adequate test. We initially settled on two 500 watt and one 400 watt cartridge heaters, which were mounted into recessed holes located beneath the three stationary balls. These holes were part of the original Allison-Diesel design. The cartridge heaters would increase the temperature of the entire test section from room temperature to 225°C in approximately fifteen minutes. The surface temperature of the cartridges did not exceed 450°C (the safe limit). Additionally heat was supplied by a flow of argon, which was preheated by passing through a (Convectronics Style 007-10134) fluid heater before entering the test section. Readings from a thermocouple positioned against one of the stationary balls are used to regulate test section temperature. This thermocouple is not in the direct flow of either the heated argon or the ethylene. Later on the hot argon flow was replaced by the substitution of a 600 watt cartridge heater for the 400 watt cartridge heater, since the argon flow diluted the ethylene flow too much.

Copper screening, which acts as a flame arrestor, was mounted for safety around all hot test section elements. The maximum unlubricated four-ball test temperature was found to be around 600°C, and the maximum lubricated (i.e. with ethylene flow) test temperature was approximately 550°C.

From previous work by Lauer and Bunting [7] it was known that nickel and nickel oxide - plating enhances carbon formation on steel. Therefore preliminary experiments were carried out with nickel-plated steel.

Prenucleation section

The same method of carbon nucleation or prenucleation (Fig. 1) was used in both the pin-on-disc and the four-ball tester. A coil of fresh nichrome wire electrically heated by a current of 11 amperes worked well. The wire temperature was estimated by attaching a thermocouple junction to the wire with "Sauereisen" cement and found to be 800°C in the steady state. This temperature is similar to the estimated flash temperatures between two sliding surfaces of silicon nitride. The wire was positioned originally near the exit nozzle. Later it was placed within the ethylene line 30 cm away from the nozzle. The optimum position has not yet been established.

Every time an experiment was terminated, the nichrome wire coil, now covered with carbon, had to be replaced. Yet it would work well for at least an hour when a test was continued. since cooling and shutting off the ethylene flow invariably brought oxygen to the wire surface, whether carbon-coated or not, this circumstance could be responsible for the loss of effectiveness.

EXPERIMENTAL RESULTS

Most of the tribological data gathered concerned wear with silicon nitride surfaces except for a few experiments where steel and nickel- or nickel-oxide plated steel was used for comparison. Because of the applied nature of this research, surface analysis, mainly Raman spectroscopy, was not a major objective but it was routinely used to demonstrated the presence of carbon and to indicate its nature. Ethylene gas or rather a mixture of ethylene and argon was the source of carbon lubricant generation in all cases. In accordance with our objective the ambient temperatures of the friction contacts were generally around 500°C and the contact pressures around 2.2 GPa. A pin-on-disc tribometer was the basic tool to establish the parameters for best bearing performance. Both sliding and rolling bearings were simulated with the modified four-ball tester.

Pin-on-disc sliding tests

Pin-on-disc sliding experiments were carried out to verify the validity of the concept under representative bearing conditions.

Fig. 3 shows some representative friction traces of short (up to 10 minutes) duration. Without lubrication the friction coefficient was constant at about 0.6. With ethylene flow the friction coefficient drifted slowly downward to reach about 0.2. The initial variations per cycle fluctuated strongly during the first half of the experiments, but became smaller later on. When a heated nichrome wire was placed between the ethylene injection nozzle and the friction contact, and the flow of ethylene was started, the friction coefficient dropped rapidly but the noise fluctuations thereafter were high. On the other hand, when the wire was placed 30 cm upstream, the friction coefficient dropped rapidly and the noise level, except for one exceptional region, remained low. The last experiment was the same as the previous one but the current to the heated wire was discontinued after

300 seconds. This discontinuing reduced the noise and maintained it at a low level.

The behavior of these friction traces can be explained pragmatically in terms of carbon nucleation and growth rates and temperature variations in the contact as lubricating carbon is formed. As soon as more carbon is formed than is needed for steady-state lubrication, the friction coefficient and therefore the contact temperature will decrease. But the decrease in contact temperature will reduce the rate of carbon formation and therefore the effectiveness of lubrication. The friction coefficient will rise again, the temperature will increase, more carbon will be produced and the cycle will start over again. When prenucleation is proper, the rate of carbon formation in the friction contact will just balance the rate of carbon loss by wear and these cyclic fluctuations will be absent. finding the balance will require more research.

Fig. 4 shows similar friction traces when the experiments were extended to one hour.

The pin wear scar areas corresponding to the friction traces of Fig. 3 and also listed there numerically are shown graphically in Fig. 5 for emphasis. Without the prenucleating wire wear was still greatly reduced over the unlubricated case but prenucleation provided additional improvement.

A comparison of the wear scar area after 10 minutes with that after one hour (Fig 6) shows only a small increase for the longer time. The wear rate is decreasing with test duration.

Short time (10 minute) trends of pin wear rate with bulk temperature and test time are shown in Figs. 7 and 8. A temperature of at least 400°C and a test time in excess of 250 seconds were required to put sufficient carbon into the contact (no prenucleation was used). Analogously no effect on wear was seen when ethylene was introduced into the contact (at 500°C, 2.43 GPa, 180 sec test

duration) at sliding speeds in excess of 5 cm/sec: the dwell time was too short to deposit adequate amounts of lubricating carbon.

Four-ball sliding and rolling tests at low rotational speeds

Table I contains results of sliding tests with steel balls conducted to establish a baseline. The improvement by ethylene (non-prenucleated) was greatest for uncoated 52100 steel while the nickel-coated steel showed only marginal improvement. The nickel-oxide coated balls gave erratic results presumably because of uneven coatings. However, in absolute terms the nickel-coated balls had the lowest wear when lubricated with ethylene carbon.

Rolling tests were performed at two different pressures under the conditions listed in Table II. The average widths of the wear track on the driven ball and on the races were measured and compared for the lubricated and unlubricated conditions. The surface profiles about the wear track were also obtained with a stylus profilometer. Clearly ethylene lubrication was effective. The decrease of track depth on the races with lubrication turned out to be substantial. Fig. 9 shows the different wear track depths on the races by bar graphs. These data are the first that demonstrate the applicability of our concept to rolling friction.

The effectiveness of our lubrication with rolling balls was still very obvious when silicon nitride balls were substituted for the nickel-coated steel balls. The results with the nickel-plated or unplated steel races are summarized in Table III and shown more clearly in Fig. 10. There is another interesting aspect to the data of Figs. 9 and 10: Without ethylene flow, even though the wear track widths were essentially the same for metal and ceramic balls, the wear track depths in the races were much less with the ceramic balls, i.e. roughly one-third as big. With ethylene lubrication, the factor was only about one-half. Undoubtedly the higher wear with surfaces of the same material rubbing against one another is a

reflection of the well-known adhesion phenomenon. Carbon produced by ethylene helps to counter it.

Tests with silicon-nitride flats in the modified four-ball wear tester

Tables IV a,b,c,d list wear results in terms of average wear scar areas on the flats (a) with and without prenucleated ethylene, (b) with prenucleated ethylene at different bulk temperatures, (c) at different rotational (sliding) speeds and (d) at different ethylene/argon ratios. Ethylene lubrication, especially when prenucleated, was very effective. A higher bulk temperature and a higher sliding speed increased the area of the wear scar and, interestingly, a higher ethylene/argon ration also increased the area of the wear scar, though only slightly. Speed and flow ratios could also have changed the surface temperatures and it was not possible to maintain the bulk temperatures at an exactly constant level. These data must therefore be considered exploratory. Fig. 11 compares the effects of no ethylene, and of both nucleated and unnucleated ethylene. The effects are certainly large.

The results of these experiments provided guidelines on the operating parameters to be used in the four-ball tester with only silicon nitride balls and races (see below).

Tests at rotational speeds of 1680 rpm in the four-ball tester with steel races

The only way possible for us to increase speed above 900 RPM in the four-ball tester was to replace the variable speed DC motor by an induction motor of constant speed (1680 RPM with the present pulley pair). In some of the subsequent test runs with ceramic balls and steel races strong vibrations occurred. For this reason the ceramic race was tested only at 500 RPM.

Fig. 12 shows the wear track on 52100 steel races generated by different silicon nitride rolling balls driven at 500 and 1680 RPM under the conditions stated. The lubricated wear is higher at the higher speed, but still less than the unlubricated wear at 500 RPM. It should be noted that when sliding *distances* are compared, wear at 1680 RPM is actually less than at 500 RPM because the test times were the same.

Fig. 13 is the equivalent of Fig. 12 for both 52100 nickel-coated steel balls and races. Here the wear of the wear track was less at 1680 RPM than at 500 RPM even for the same operating time. This result is in consonance with all our previous observations on the advantage of nickel surfaces.

Four-ball tests with both silicon nitride balls and races

As Fig. 14 shows, lubricated wear with silicon nitride balls and races was less than with the nickel-coated steel components. The reason for this good result is the advantage of our concept of lubrication as well as the known unsuitability of steel at these high temperatures and pressures.

Characterization by Raman spectroscopy of pyrolytic carbon deposited on silicon nitride pins (small bearing balls) run against silicon nitride discs in the presence of a flow of ethylene

The series of spectra of Figures 15 and 16 are included in this paper because they are consistent with the theory of carbon particle growth with time. Raman spectra were obtained of many of the carbons deposited in our experiments, but their detailed analysis in this paper is not warranted. The instrument used was an Instrument SA. Raman Microprobe, which was described in one of our publications [8]. The two principal Raman bands of carbon have been called D (the low frequency band at ~ 1360 cm^{-1}, D for diamond or disorder)

compared to the G band has been considered evidence of small graphite-like crystallites. Clearly the D/G band intensity ratio decreased with run time, thereby implying crystallite growth.

When the ethylene flow and sliding of the pin on the disc continued the D peak would rise compared to the G peak or the D/G ratio would increase. Grinding of the carbon could be the mechanism in that case. Figs 15 and 16 are illustrative of the trend.

Raman spectra of carbons have been studied extensively in recent years, primarily by the makers of carbon-sputtered, hard computer discs and the reader is referred to the voluminous literature in this area [9].

DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS

The objectives of this program of applied research have been met more closely than we had expected ourselves. Our concept of solid lubrication by carbon generated on ceramic tribo-surfaces by a continuous supply of a carbonaceous gas to the contact region has been validated both with a pin-on disc and a four-ball wear tester at bulk temperatures above 500°C and contact pressures between 2.2 and 2.5 GPa for both sliding and rolling friction. A new idea, prenucleation by an electrically heated wire upstream in the gas feed, to generate more carbon more rapidly has been found practical and very useful. It avoids the potential need for metal-plating of ceramic friction parts: the catalytic surface can be situated elsewhere.

Conceptually the nature of the surfaces should be immaterial, if the process of pyrolysis is homogeneous as Porter had postulated. Yet we have not been alone in finding surface effects [3]. The heated nichrome wire must also be catalytic or its being overcoated with carbon in the presence of oxygen should not have mattered. Perhaps a non-catalytic tungsten wire at a higher temperature would be equally effective. Platinum or palladium might be more effective. The nature of the tribosurfaces is also important and not just the flash temperature in the contact. Our earlier pin-on-disc experiments [1] have shown that ceramics with higher thermal conductivity, such as silicon carbide or nitride, are more effective in our process than those of lower thermal conductivity, such as zirconia. Yet the flash temperatures are certainly higher for zirconia than for silicon nitride under equal conditions. Perhaps it is a thermal gradient that is important here because of better carbon condensation. This aspect should be paid more attention.

From the practical as well as theoretical point of view carbonaceous gases other than ethylene should be explored. High on our list are carbon monoxide and carbon dioxide as they are the major constituents of engine exhaust. Admixtures of hydrogen to hydrocarbons should be studied even though hydrogen is always a product of pyrolysis. But some excess hydrogen might accelerate the reaction. Water vapor could have a similar influence. Partly oxygenated hydrocarbons such as methanol could also be helpful according to Bachmann's diagram for low pressure carbon production [10]. Our earlier work has shown that alcohols can be effective in our process. It has also shown that a silicon carbide can be formed on sialon tribo-surfaces.

The identification of the carbon nuclei in the ethylene stream presents an intriguing problem. It was already posed by Porter, who suggested C_2, CH+, acetylene, etc., but never solved. We should also be in a good position to estimate the life time of these nuclei by varying the wire-to-contact distance and the flow rates.

More attention should be paid to the gas flow and the heating of the four-ball test section. We are now at or near the upper temperature limit. More powerful cartridge heaters will warp the steel structure. Heated argon requires high flow rates which dilute the ethylene feed in its present configuration. However, in any case the housing could not be heated more than now. Substitution of quartz or lava for some of the steel might prove effective. Radiation heating should be considered.

While the wear in the presence of ethylene-generated surface carbon is substantially lower than in its absence, the wear is still high compared to that encountered in liquid-lubricated ball bearings at operating temperatures below 350°C. However, the results reported here are just a beginning toward practical lubrication at 500°C or higher by our concept. Plans for improvement have been

mapped out. They include: (i) relocation of the gas inlet nozzle in the four-ball tester, (ii) more prenucleation, e.g. by several heated wire coils, (iii) adjusting the period of prenucleation, (iv) use of carbonaceous gases other than ethylene and gas mixtures, (v) variation of surface finishes of moving parts, (vi) nickel or other ion implantation or coating of ceramic parts, (vii) different catalytic surfaces or sequences of catalytic surfaces for prenucleation, (viii) variation of operating parameters, such as sliding and rolling speeds, gas flow rates, mixture ratios, and (ix) many other parameters not yet defined. By these approaches improvements of wear of two orders of magnitude should be possible.

Preliminary pin-on-disc sliding tests employing acetylene gas, or carbon monoxide/hydrogen, carbon monoxide/hydrocarbon or carbon dioxide/hydrogen gas mixtures as sources of replenishable lubricating carbon have proved promising. In particular, sliding performance under the carbon monoxide/hydrogen mixture has equaled that of ethylene. The exemplary wear reduction resulting from the carbon monoxide mixture has also been demonstrated in high-temperature rolling tests employing silicon nitride balls upon 52100 steel races. It is proposed that carbon monoxide, carbon dioxide, various engine exhaust hydrocarbons, and exhaust mixtures be evaluated for the high-temperature lubrication of both sliding and rolling elements, particularly rolling elements consisting of silicon nitride balls as well as races.

It is also proposed that rolling tests be performed under the more severe conditions experienced by bearings in IHPTET engines. Lubrication for extended periods should be demonstrated at temperatures of at least 650°C and rotational speeds of at least 10,000 rpm. The higher speeds will require an alteration of the gear ratio between the 4-ball spindle and drive motor, as well as some possible machining and truing of the 4-ball spindle itself.

During 4-ball tests employing ethylene at a volume flow rate of 2 l/min, the maximum temperature attainable within the rolling contact has been approximately 590°C, When employing carbon monoxide, which must flow at a higher rate, the added convection limits the maximum temperature to roughly 500 °C. It is clear that, at the very least, an increase in cartridge heater power will be necessary to attain temperatures in excess of 600°C. As previously mentioned, the 4-ball housing currently is comprised of steel. Some reworking of this housing may also be necessary to achieve satisfactory performance at the desired temperatures and speeds.

This prospective research would be a large step forward towards the application of a novel extended duration solid lubrication scheme to a high-temperature bearing application.

ACKNOWLEDGEMENT

We wish to thank our sponsors and acknowledge the support and funding for the work described in this report which was provided by NASA-Lewis Research Center. The New York State Energy Department Authority and the National Science Foundation under Grant MSS-9015989.

Dr. Lauer's co-workers were Brian L. Vicek and B. Sargent.

REFERENCES

1. Lauer, J.L. , and Dwyer, S.R., "Tribochemical Lubrication of Ceramics by Carbonaceous Vapors," Tribology Transactions 34 (4), 521-528 (1991).

2. Porter, G., "The Mechanism of Carbon Formation," Combustion Research and Reviews, 108-123 (1955).

3. Banergee, B.C., Hirt, T.J., and Walker, P.L., Jr., "Pyrolytic Carbon Formation from Carbon Suboxide," Nature 192, 450-451 (1961).

4. Tesner, P.A., "Kinetics of Pyrolytic Carbon Formation," in Chemistry and Physics of Carbon (P.A. Thrower, ed.), Vol. 19, pp. 65-161, New York, Marcel Dekker, Inc., New York, 1988.

5. Johnson, W.L., "The Characterization of Graphitic and Non-graphitc Carbon by Laser Microprobe Analysis, Microbeam Analysis 26, p. 26 (1986). Published by San Francisco Press.

6. Klaus, E., Duda, J., and Wu, T., "Lubricated Wear of Silicon Nitride," Lubrication Engineering, 47(8), 679-684 (1991).

7. Lauer, J.L., and Bunting, B.G., "High Temperature Lubrication by Catalytically Generated Carbon," Tribology Transactions 31(3), 338-349 (1988).

8. Lauer, J.L., and DuPlessis, L., "Relation between Deposition Parameters, Structure and Raman Spectra of Carbon Overcoats on Magnetic Storage Discs," STLE, SP-29, 71-78 (1990) (B. Bhushan, ed.)

9. Knight, D.S., and White, W.B., "Characterization of Diamond Films by Raman Spectroscopy," J. Mater. Res. 4(2), 385-393 (1980).

10. Bachmann, P.K., Leers, E., and Lydtin, H., "Towards a General Concept of Diamond Chemical Vapor Deposition," Diamond and Related Materials, 1, 1-12 (1991).

LIST OF TABLES

TABLE I

Average Wear Scar Areas of the Stationary Balls in the Four-Ball Tester after Runs without and with Ethylene

Ball Materials	Wear Scar Area (mm^2)	
	Without Ethylene	With Ethylene
52100 steel	2.42	0.82
same steel but Ni-plated	0.68	0.40
same steel but NiO-plated	0.21*	0.46

*result in doubt

NOTE: The parameters were: 400°C, 2.26 GPa, 200 rpm, 300 second test duration.

TABLE II

Wear Scar Areas after Rolling Tests with Nickel-Coated 52100 Steel Balls and Races in Four Ball Tester

Contact Pressure (GPa) and Lubrication State	Width of Wear Track on Driven Ball (mm)	Width of Wear Track on Race (mm)	Depth of Wear Track on Race (μm)
1.3 (unlubricated)	0.50	1.74	20.36
1.3 (lubricated*)	0.30	1.23	5.23
2.26 (unlubricated)	1.04	2.49	31.48
2.26 (lubricated*)	0.42	2.33	7.18

*lubricated by carbon deposits from 2.0 l/min ethylene with 2.0 l/min argon nucleated by passing over a heated nichrome wire.

NOTE: The parameter were: Ni-coated 52100 steel balls and races, initial bulk temperature 575°C, 500 rpm, one hour test duration.

TABLE III

Wear Scar Areas after Rolling Tests with Silicon Nitride Driven Ball and Ni-Coated or Uncoated 52100 Steel Rolling Balls and Races

Rolling Balls and Races	Width of Wear Track on Driven Ball (mm)	Width of Wear Track on Race (mm)	Depth of Wear Track on Race (mm)
Ni-coated 52100 Steel			
(a) unlubricated	2.37	1.92	7.18
(b) lubricated*	1.79	0.46	2.46
Uncoated 52100 Steel			
(a) unlubricated	2.48	2.80	6.47
(b) lubricated*	0.80	1.70	2.63

*lubricated by carbon deposits from 2.0 l/min ethylene with 2.0 l/min argon nucleated by passing over a heated nichrome wire.

NOTE: The parameter were: Initial bulk temperature 575°C, 500 rpm, one hour test duration.

TABLE IV

Wear Scar Areas on Silicon Nitride Flats of Modified Four-Ball Wear Tester after 10-minute Runs against a Silicon Nitride Ball at 2.66 GPa Contact Pressure with and without Prenucleated Ethylene

(a) Showing effect of prenucleated ethylene,

Bulk Temperature (°C)	Ethylene/Argon Flow Rates (l/min)	Nucleating Wire Temperature (°C)	Average Wear Scar Area (mm^2)
500	0.0/2.0	24	4.78
517	0.5/2.0	24	2.04
510	0.5/2.0	800+	1.73

(b) Showing effect of bulk temperature,

Bulk Temperature (°C)	Average Wear Scar Area (mm^2)
510	1.76
572	2.17

NOTE: Prenucleated ethylene was introduced into the conjunction region

(c) Showing effect of sliding speed at 570°C

Rotional Speed (rpm)	Average Wear Scar Area (mm^2)
100	1.42
200	2.17

NOTE: Ethylene/argon flow rates were 0.5/2.0 l/min.

(d) Showing effect of ethylene dilution by argon at 500°C with prenucleated ethylene

Bulk Temperature (°C)	Ethylene/Argon Flow Rate (l/min)	Average Wear Scar Area (mm^2)
500	0.0/2.0	4.78
510	0.5/2.0	1.76
507	1.0/2.0	1.93
537	2.0/2.0	2.15

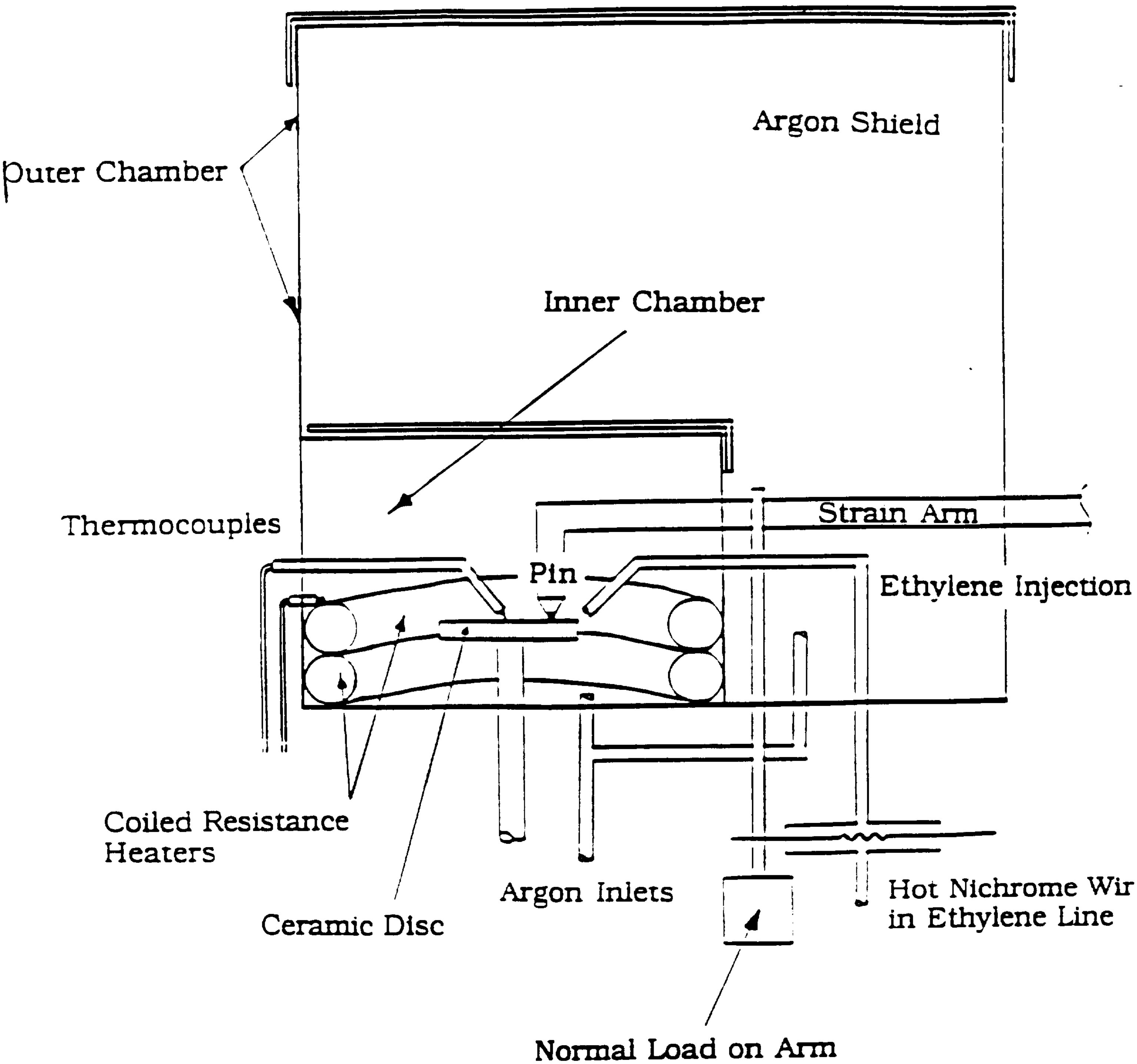


Fig. 1 Schematic of pin-on-disc tribometer

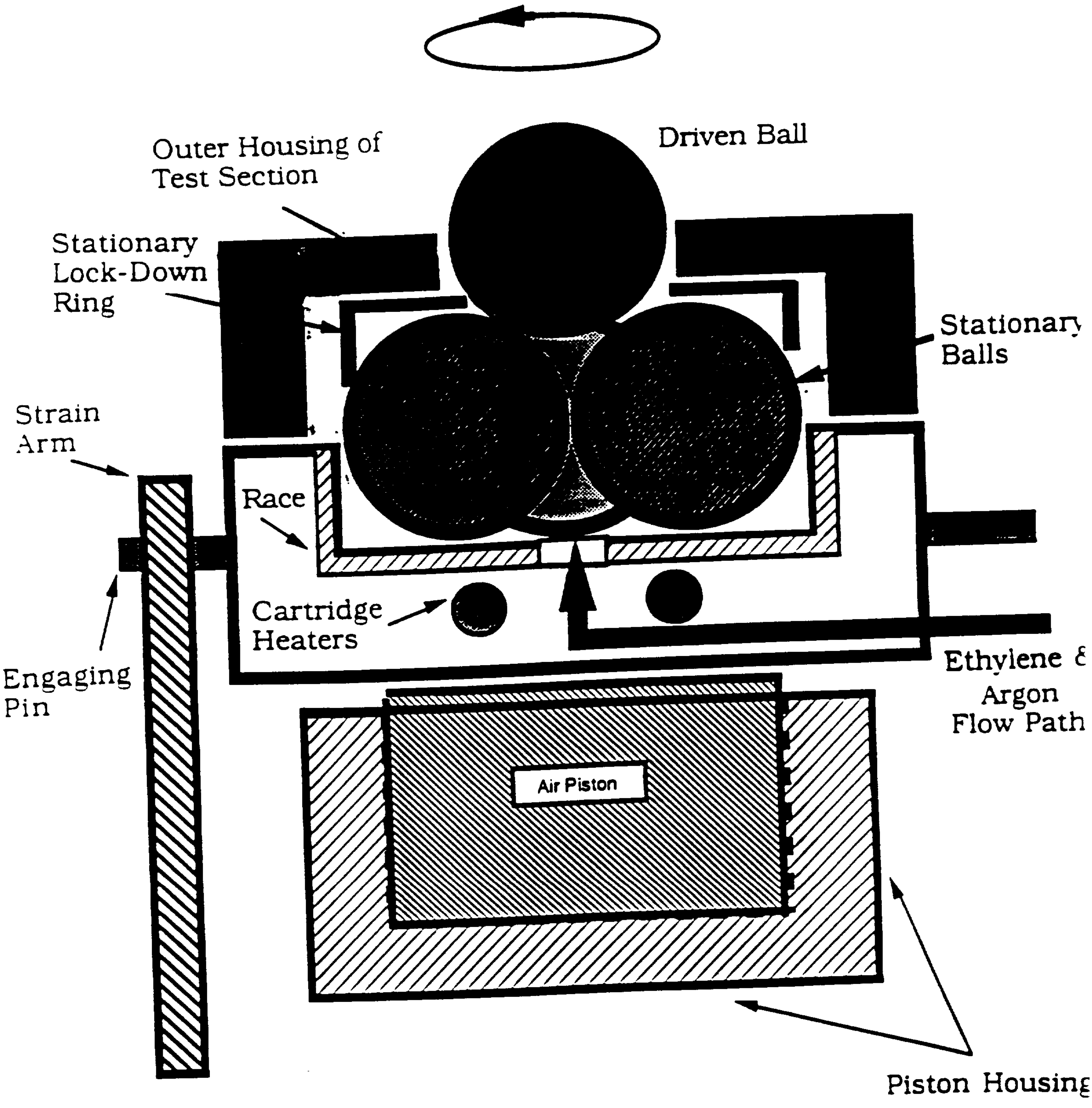


Fig. 2a Basic setup of high temperature four-ball wear and friction tester with lower three balls stationary.

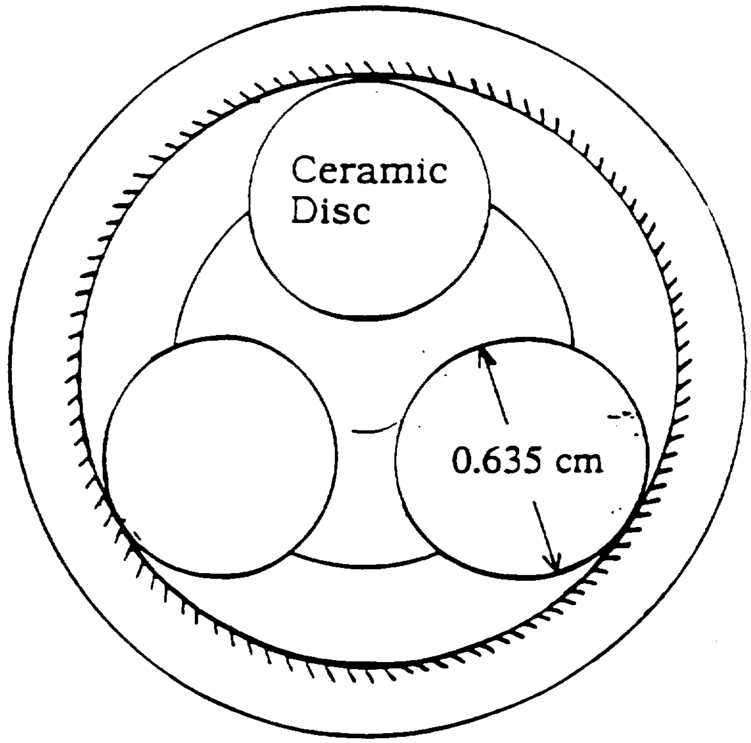


Fig. 2b Top view of modification showing the location of flat plates which replace lower bottom balls

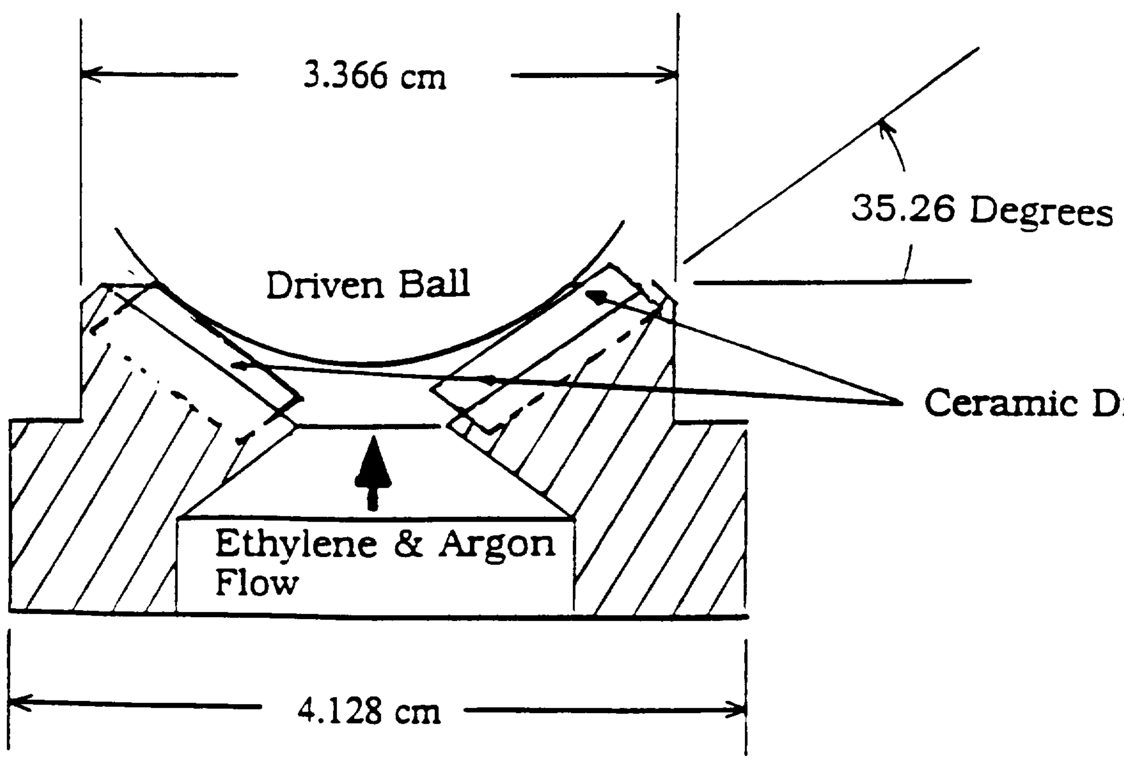


Fig. 2c Side view of 2b.

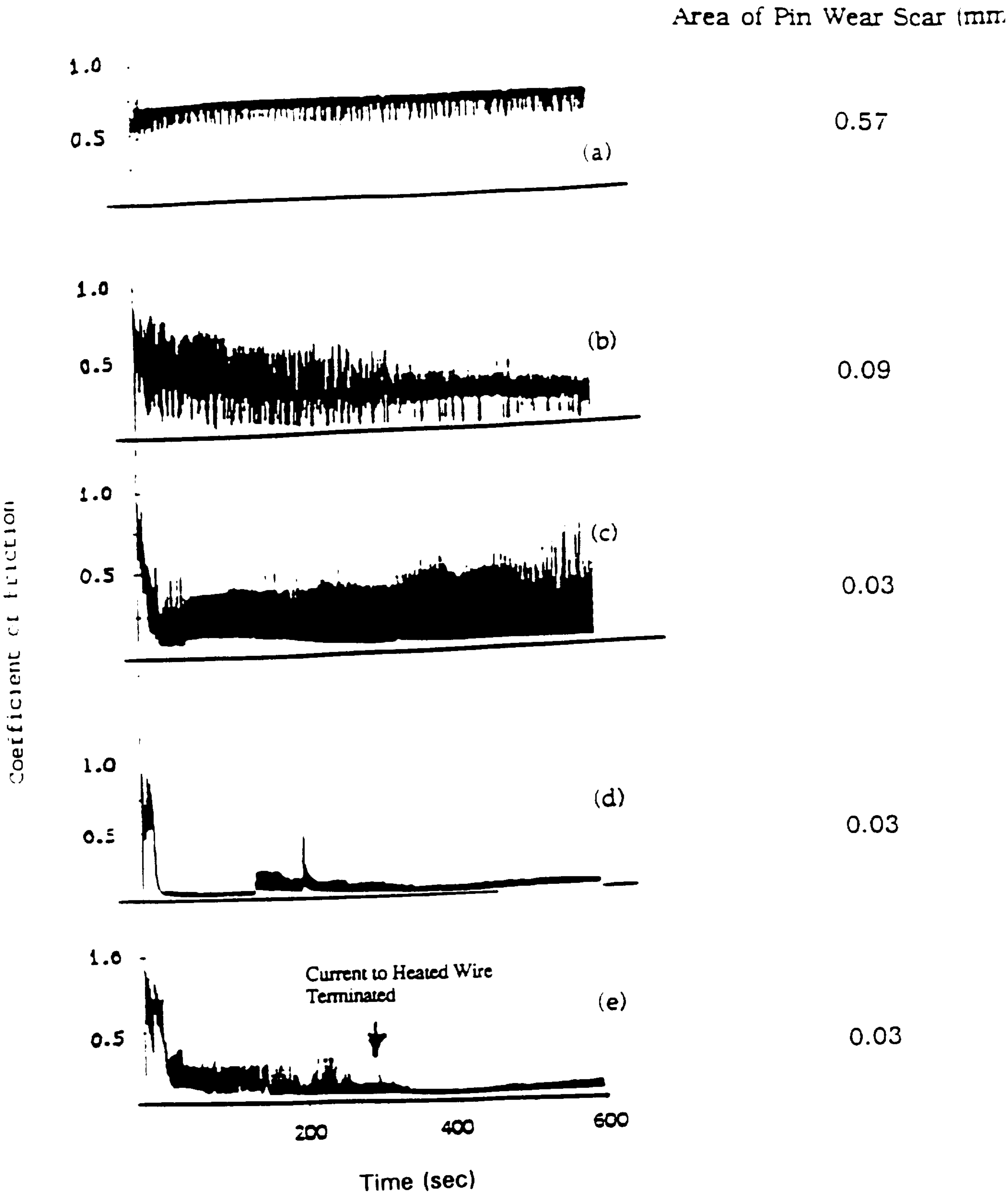


Fig 3. Silicon nitride pin-on-disc friction traces of 10 minutes duration and corresponding wear scar areas on the pin.

(a) no ethylene flow,

(b) ethylene flow, no prenucleation,

(c) ethylene flow and prenucleation between nozzle and contact,

(d) ethylene flow and prenucleation 30cm ahead of nozzle.

(e) same as (d) but prenucleation stopped after 300 seconds.

CONDITIONS: bulk temperature: 520°C, contact pressures: 2.66GPa, and sliding speed 5 cm/sec.

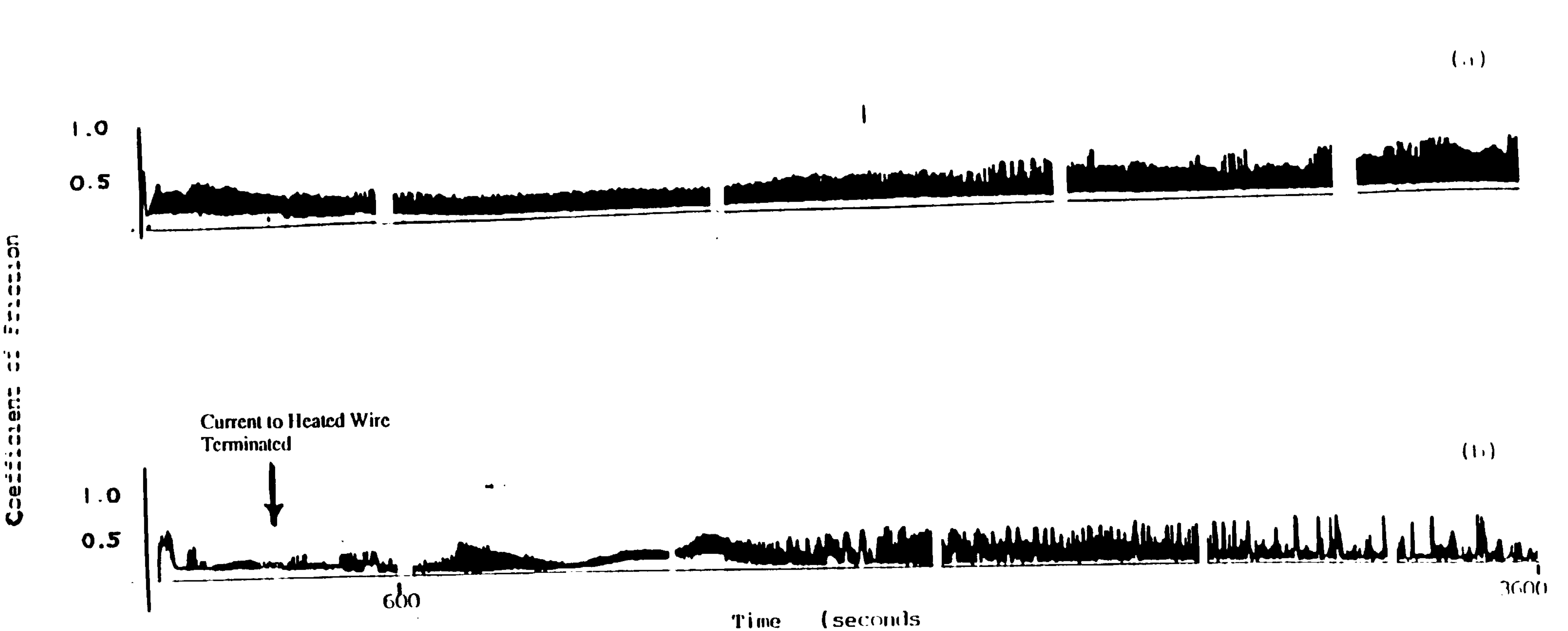


Fig 4. Silicon nitride pin-on-disc friction traces of 1 hour duration with prenucleated ethylene.
(a) continuous prenucleation,
(b) prenucleation terminated after 300 seconds.
CONDITIONS: bulk temperature 520°C, contact pressure: 2.66 GPa, sliding speed: 5 cm/sec.

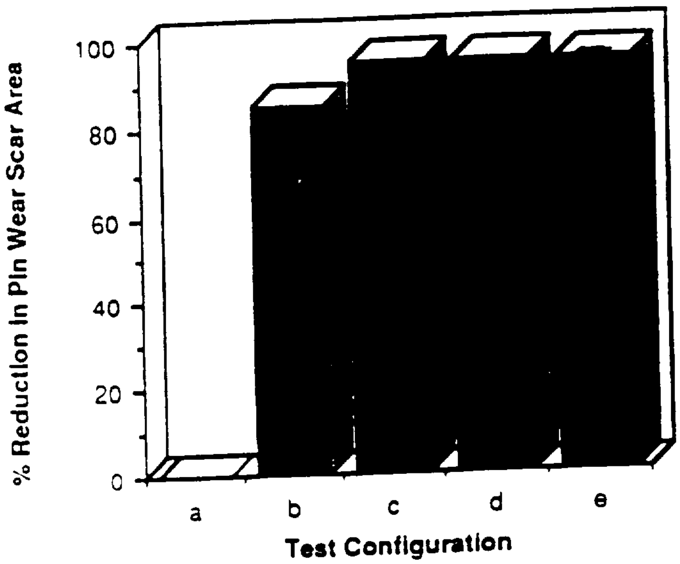


Fig. 5. Percent Reduction in Wear Scar Area (as compared to unlubricated values). Silicon nitride pin slid against a silicon nitride disc for 10 minutes.

(a) No ethylene flow.
(b) Ethylene flow, no prenucleation.
(c) Ethylene flow and prenucleation between nozzle and contact.
(d) Ethylene flow and prenucleation 30 cm ahead of nozzle.
(e) same as (d) but prenucleation stopped after 300 seconds.

CONDITIONS: bulk temperature 520°C, contact pressure 2.66 GPa, and sliding speed 5 cm/sec.

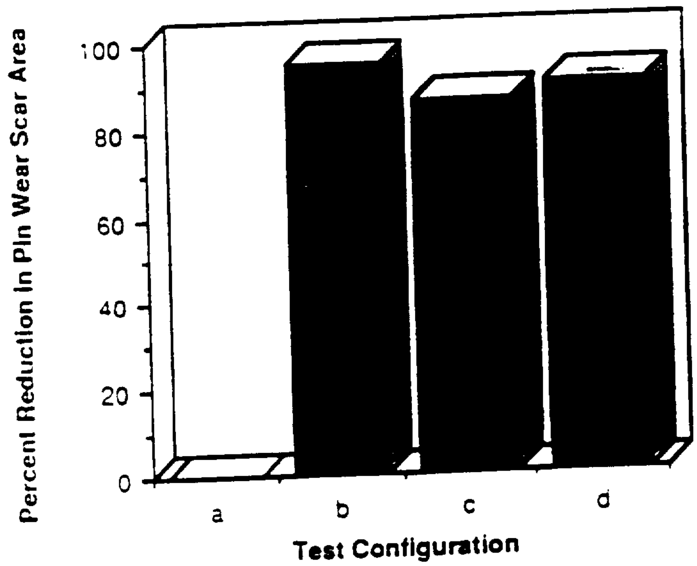


Fig. 6. Percent Reduction in Wear Scar Area (as compared to unlubricated values). Silicon nitride pin slid against a silicon nitride disc for 10 minutes and 60 minutes.

(a) No ethylene flow. Total test time 10 minutes.
(b) Ethylene flow and prenucleation 30 cm ahead of nozzle. Total test time 10 minutes.
(c) Ethylene flow and prenucleation 30 cm ahead of nozzle. Total test time 60 minutes.
(d) As (c) but prenucleation terminated after 300 seconds.

CONDITIONS: bulk temperature 520°C, contact pressure 2.66 GPa, and sliding speed 5 cm/sec.

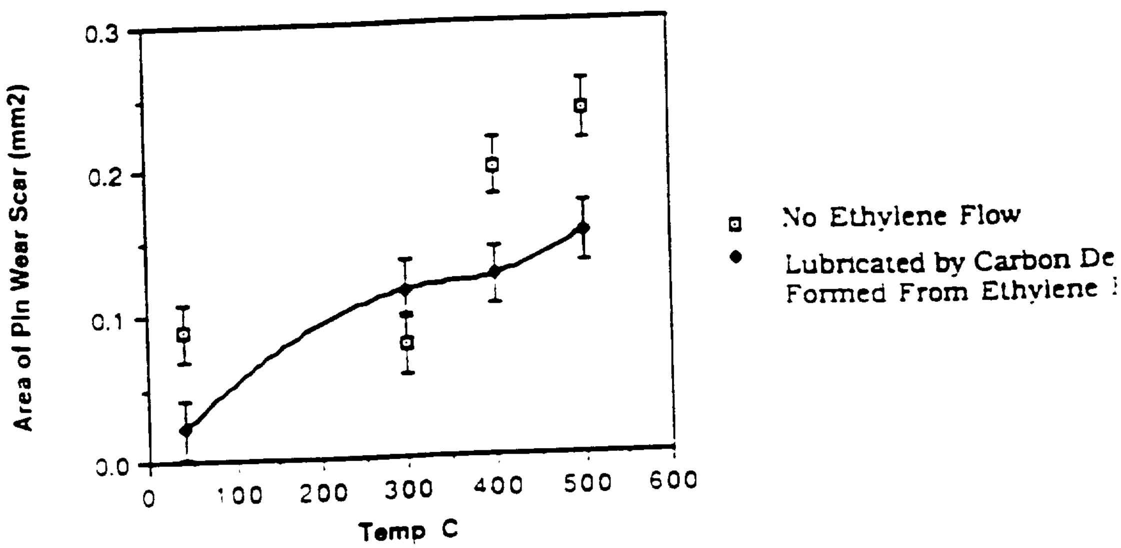


Fig. 7. Changes in silicon nitride pin wear with increasing temperature. CONDITIONS: Silicon nitride pin on silicon nitride disc. sliding speed: 5 cm/sec. contact pressure: 2.43 GPa. lubrication by carbon deposits generated from exposure to 7.5 l/min of ethylene for 230 seconds.

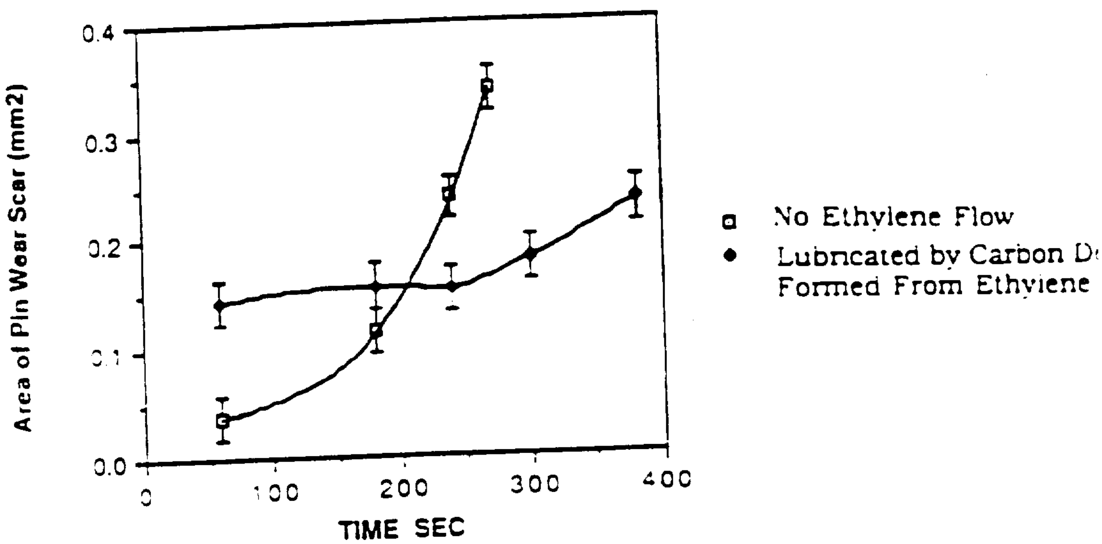


Fig. 8. Changes in silicon nitride pin wear with increasing time. CONDITIONS: Silicon nitride pin on silicon nitride disc. sliding speed: 5 cm/sec. contact pressure: 2.43 GPa. bulk temperature: 500°C. lubrication by carbon deposits generated from exposure to 7.5 l/min of ethylene for 230 seconds.

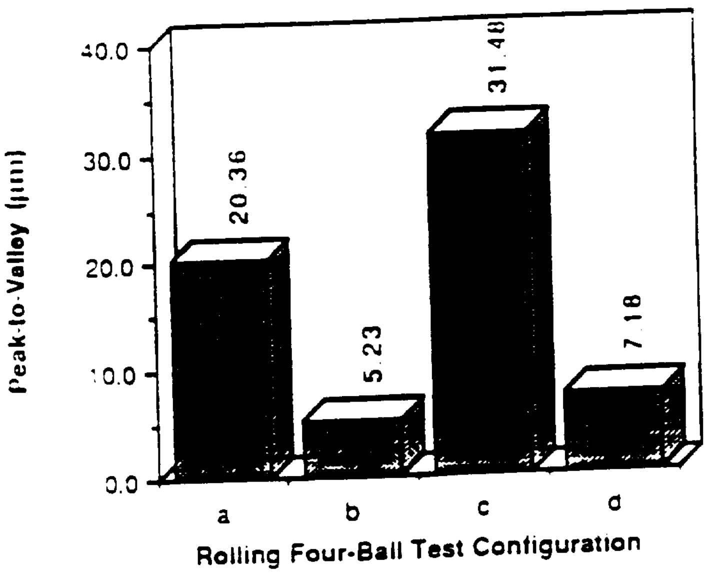


Fig. 9. Depths of wear track on the Ni-plated 52100 steel races used in four-ball rolling tests.

(a) contact pressure: 1.3 GPa. no ethylene flow.
(b) contact pressure: 1.3 GPa. and prenucleated ethylene flow.
(c) contact pressure: 2.26 GPa. no ethylene flow.
(d) contact pressure: 2.26 GPa. and prenucleated ethylene flow

CONDITIONS: Rolling and driven balls: Ni-plated 52100 steel. bulk temperature. 575°C. linear speed: 19.4 cm/sec (500 rpm). test duration: 1 hour.

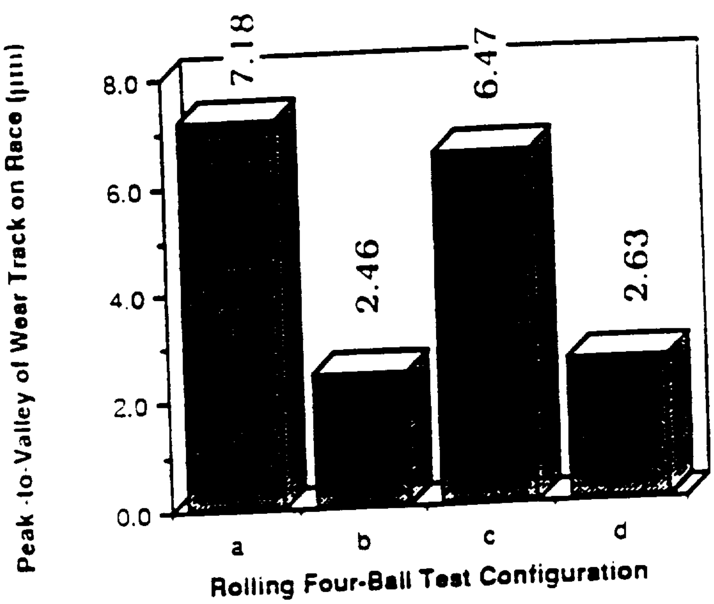


Fig. 10. Depths of wear tracks on the 52100 steel (Ni-plated or not) races used with silicon nitride balls in 1-hour rolling tests.

(a) no ethylene flow. Ni-plated race.
(b) nucleated ethylene flow. Ni-plated race.
(c) no ethylene flow. unplated race.
(d) prenucleated ethylene flow. unplated race.

CONDITIONS: bulk temperature: 575°C. contact pressure 2.26 GPa. linear speed: 19.4 cm/sec (500 rpm).

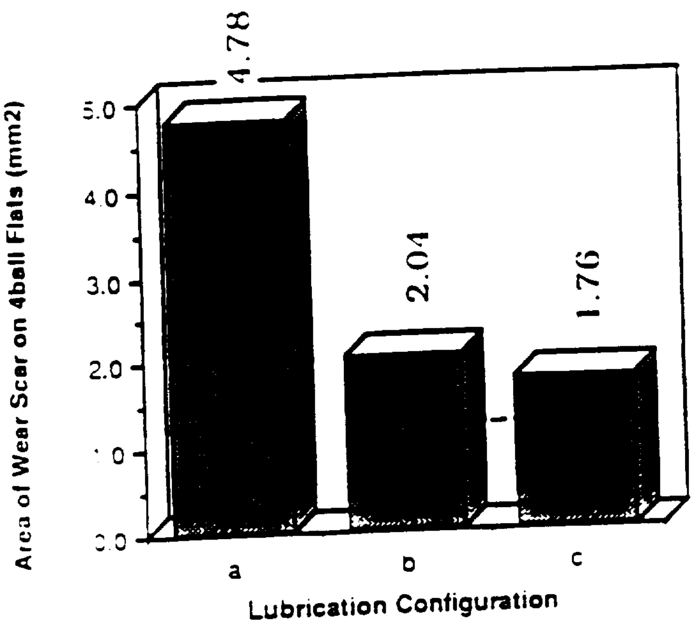


Fig. 11. Wear scar area on silicon nitride flats of modified four-ball sliding tests.

(a) No ethylene flow.
(b) ethylene flow, and
(c) prenucleated ethylene flow.

CONDITIONS: bulk surface temperature: 575°C, contact pressure 2.66 GPa, linear speed: 7.8 cm/sec (200 rpm), run time 5 minutes.

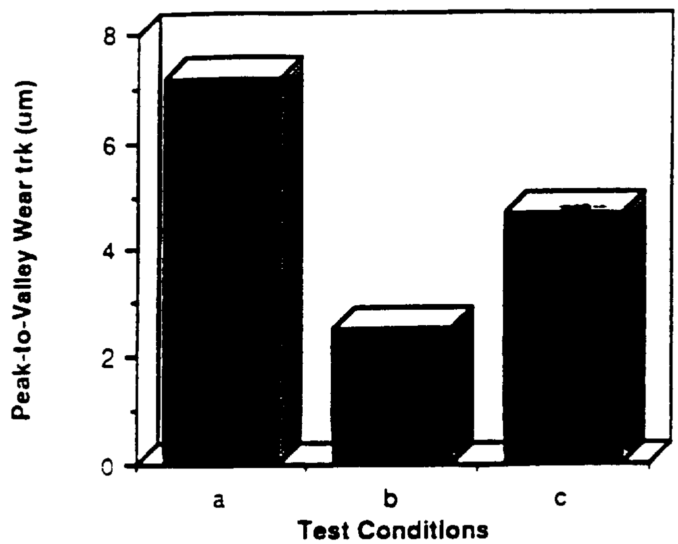


Fig. 12 Peak-to-valley depth of wear track obtained from 52100 races tested with rolling Si3N4 balls at bulk temperatures of 520°C, initial contact pressure of 2.2 GPa, total test time of 3600 seconds, and

a. unlubricated, and 500 rpm
b. lubricated by nucleated ethylene, and 500 rpm
c. lubricated by nucleated ethylene, and 1680 rpm

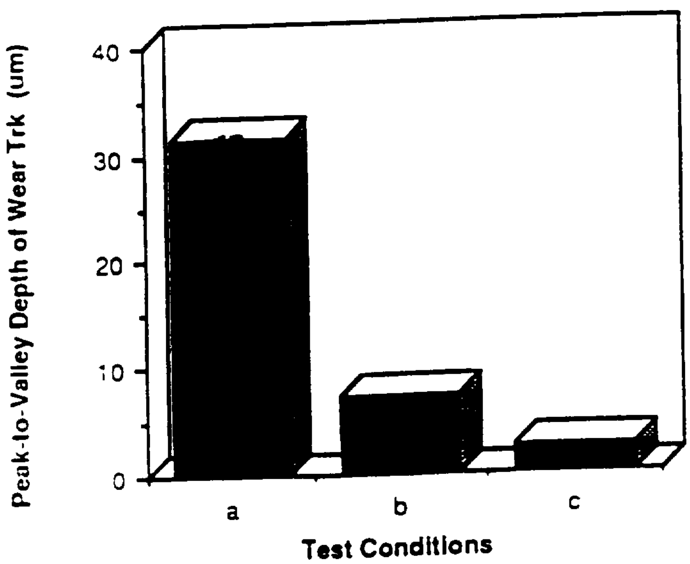


Fig. 13 Peak-to-valley depth of wear track on nickel-plated 52100 races tested with rolling nickel-plated 52100 balls at bulk temperatures of 520°C, initial contact pressure of 2.2 GPa, total test time of 3600 seconds, and

a. unlubricated, and 500 rpm
b. lubricated by nucleated ethylene, and 500 rpm
c. lubricated by nucleated ethylene, and 1680 rpm

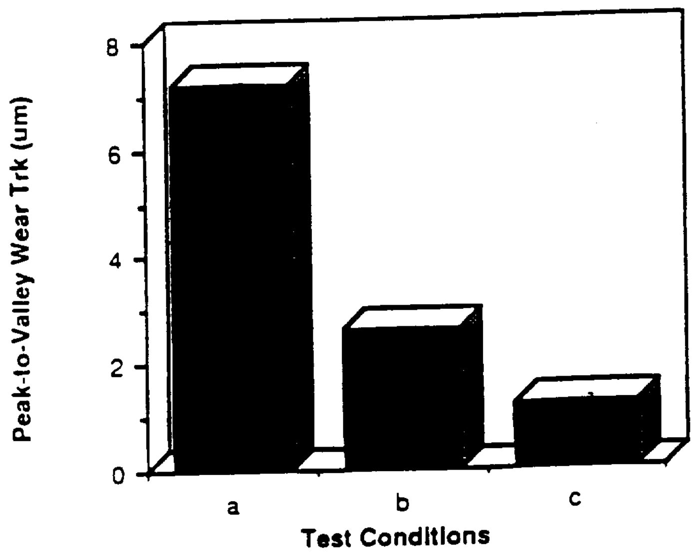


Fig. 14 Peak-to-valley depth of wear track on nickel-plate races tested with rolling balls at bulk temperatures of 520°C, initial contact pressure of 2.2 GPa, 500 rpm, total test time of 3600 seconds, and

a. Ni-plated 52100 balls and Ni-plated 52100 races lubricated by nucleated ethylene
b. Silicon nitride balls and 52100 races lubricated by nucleated ethylene
c. Silicon nitride balls and silicon nitride races lubricated by nucleated ethylene

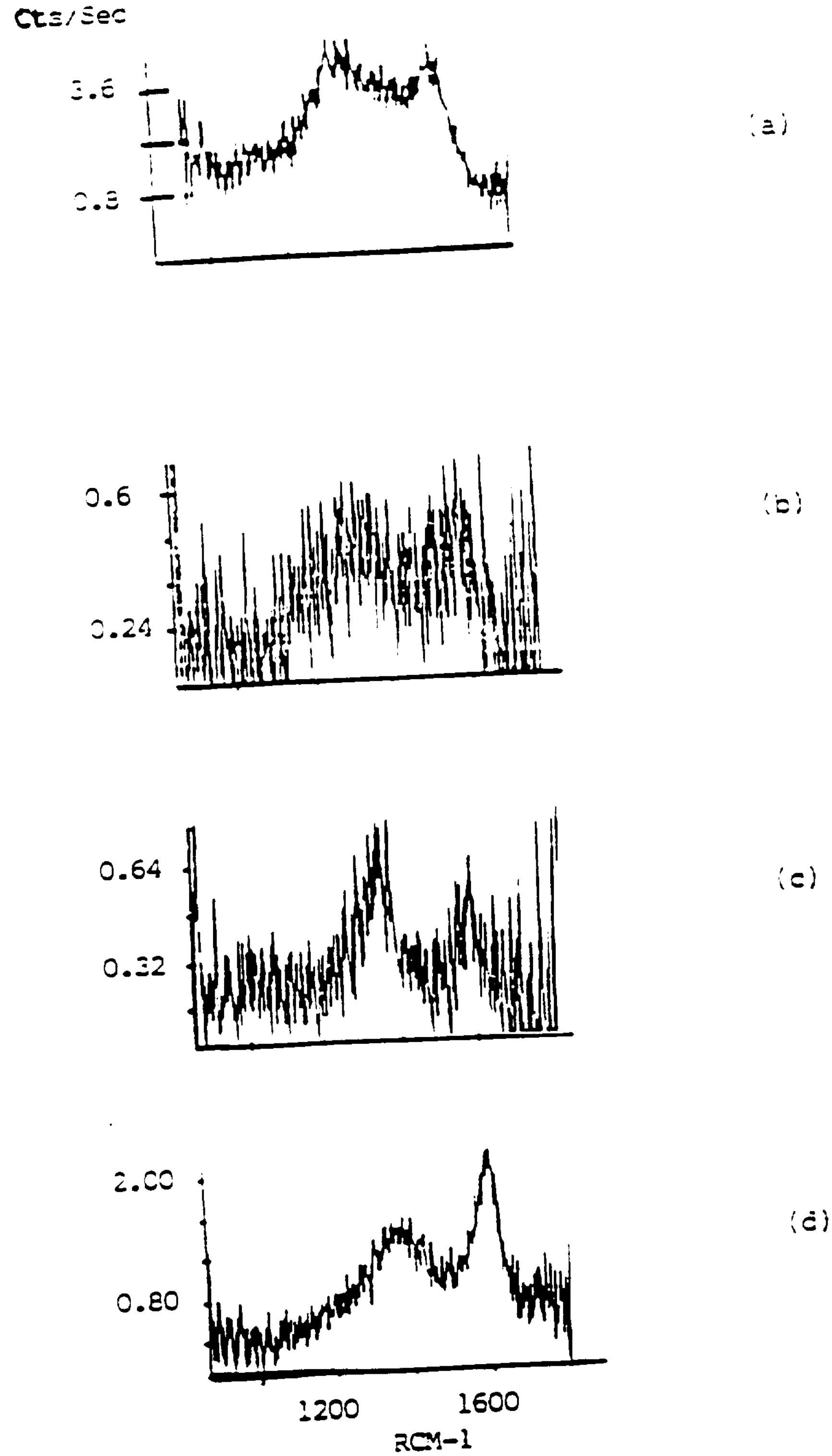
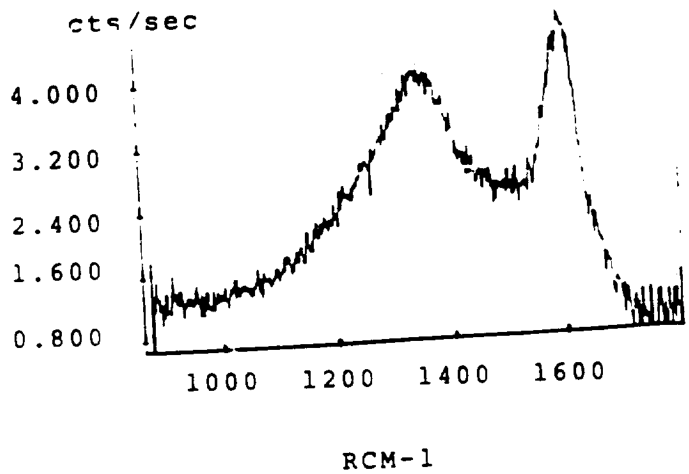


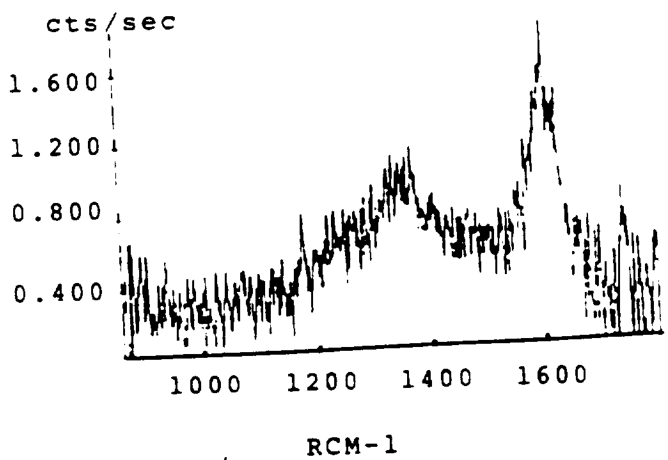
Fig. 15 Raman spectra of the carbon deposited on the wear scar of a silicon nitride pin slid against a silicon nitride disc.

a. 50 seconds of run time.
b. 180 seconds of run time (brown deposit on surface).
c. 180 seconds of run time (black deposit on surface). and
d. 240 seconds of run time.

CONDITIONS: bulk temperature: 500°C. contact pressure: 2.21 GPa. sliding speed: 5 cm/sec. and wear contact exposed to ethlyene.



(a)



(b)

Fig. 16 Raman spectra of the carbon deposited on the wear track of the silicon nitride plates that were in contact with two of the pin whose spectra are shown in Figure 15.

a. 180 seconds of run time, and
b. 240 seconds of run time

CONDITIONS: bulk temperature: 500°C, contact pressure: 2.21 GPa, sliding speed: 5 cm/sec, and wear contact exposed to ethylene.

E-8688 CR189214

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (*Leave blank*)

2. REPORT DATE
December 13, 1993

3. REPORT TYPE AND DATES COVERED
Final Contractor Report

4. TITLE AND SUBTITLE
Wear Reduction in Ceramic Bearings by Surface Generated Pyrolytic Carbon Continuously Replenished by Ethylene Gas

5. FUNDING NUMBERS
NASA Contract
NAS3-25950 Task 3

6. AUTHOR(S)
Dr. J. L. Lauer : Rensselaer Polytechnic Institute
L. C. Davis: Allison Gas Turbine Div. GM

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Rennselaer Polytechnic Institute
Troy, NY 12180-3590
Allison Gas Turbine Div. GM
Indianapolis, IN 46206-0420

8. PERFORMING ORGANIZATION REPORT NUMBER
EDR 16732

9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES)
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135-3191
Project Manager Harold H. Coe MS 77-10

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
NASA CR-189214
AVSCOM TR 92-C-032

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Unclassified - Unlimited
Subject Category

12b. DISTRIBUTION CODE

13. ABSTRACT (*Maximum 200 words*)

Sliding tests with a pin-on-disc tribometer and both sliding and rolling tests with a modified four-ball tester at bulk temperatures of about 500°C and contact pressures of about 2.2 GPa have demonstrated up to 80% reductions of friction and wear with silicon nitride surfaces when a stream of ethylene is directed into the conjunction region. The effects are even more pronounced when the ethylene is prenucleated by a flow over a coil of nichrome wire electrically heated to about 800°C and located about 30 cm upstream of the exit nozzle. Steel and Ni-plated steel are lubricated by this method even more efficiently at lower temperatures.

14. SUBJECT TERMS
Vapor Lubrication, Friction, Wear, Bearings Ethylene, Silicon Nitride, Tribometer

15. NUMBER OF PAGES
43

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
Unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT
Unclassified

20. LIMITATION OF ABSTRAC

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102